HIGHER ORDER PERTURBATION ENERGIES FOR THE 2-ELECTRON HOOKE'S LAW MODEL ATOM*

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ABSTRACT

The Rayleigh-Schrödinger perturbation energies E_n for the ground ^1S state of the Hooke law model atom are calculated through tenth order. The E_n are expressed as singly infinite sums whose terms are obtained from recurrence relations. Very slow convergence limited the method to E_{10} and below.

The results are compared with those of Midtdal (1965) for helium-like atoms, and it appears that the convergence of the Hooke series is more rapid. However, no persistent patterns are observable in the Hooke E_n through E_{10}.

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1. Introduction

The Hooke's law model for a two-electron atom is essentially a helium-like atom in which the Coulomb attraction of the nucleus is replaced by a Hooke's law force, resulting in the Hamiltonian[1]

$$H = -\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2) + \tfrac{1}{2}m\omega^2(r_1^2+r_2^2) + \frac{e^2}{r_{12}} . \qquad (1)$$

In atomic units ($e=\hbar=m=1$), letting the frequency $\omega = Z^2$, $\lambda = 1/Z$, and with the scale change $\underset{\sim}{r}_i \longrightarrow \underset{\sim}{r}_i/Z$, the Schrodinger equation can be written in the form analogous to the Z-reduced helium equation

$$\left[-\tfrac{1}{2}(\nabla_1^2+\nabla_2^2) + \tfrac{1}{2}(r_1^2+r_2^2) + \frac{\lambda}{r_{12}} - E \right]\Psi = 0. \qquad (2)$$

The Hooke model atom for helium has been studied previously by Kestner and Sinanoglu[2] andby White and Byers Brown[1] in the hope of aiding the solution of the Schrodinger equation for helium. In this report we are again concerned with the perturbation expansion of the lowest eigenvalue E in powers of λ ,

$$E = \sum_{n=0}^{\infty} \lambda^n E_n . \qquad (3)$$

There is considerable interest in this series stemming from the work of Scherrand Knight[3] and of Midtdal[4], who obtained accurate numerical approximations to the E_n for helium through 13th and 21st orders

respectively. Stillinger[5] has used these results to deduce the nature and position of the singularity determining the radius of convergence of the series. Also the most recent attempts[6] to obtain analytic solutions of the Schrödinger equation for helium lead to perturbation-like series for the eigenvalue E.

The object of the present work is to find the perturbation energies E_n for the ground state of the Hooke model. The first two energies are easy to obtain, and E_2 and E_3 have also been evaluated analytically[1]. However, although equation (2) is separable into ordinary differential equations, the exact lowest eigenvalue $E(\lambda)$ is not known analytically as a function of λ. The equations of Rayleigh-Schrödinger perturbation theory are therefore employed to find the E_n.

2. Perturbation Equations

Equation (2) is separable[1,2] in centre of mass and relative coordinates

$$\underset{\sim}{R} = (\underset{\sim}{r}_1 + \underset{\sim}{r}_2)/\sqrt{2} \quad , \qquad \underset{\sim}{r} = (\underset{\sim}{r}_1 - \underset{\sim}{r}_2)/\sqrt{2} \, ,$$

with $\Psi(\underset{\sim}{r}_1, \underset{\sim}{r}_2) = \chi(\underset{\sim}{R})\,\psi(\underset{\sim}{r})$ to give

$$\left(-\tfrac{1}{2}\nabla_R^2 + \tfrac{1}{2}R^2 - \varepsilon\right)\chi = 0, \tag{4}$$

$$\left(-\tfrac{1}{2}\nabla_r^2 + \tfrac{1}{2}r^2 + \frac{\Lambda}{r} - \epsilon\right)\psi = 0 \tag{5}$$

where $\Lambda = \lambda/\sqrt{2}$ and

$$E(\lambda) = \mathcal{E} + \epsilon(\Lambda). \tag{6}$$

The eigenvalue ϵ of (5) can be expanded as a power series in Λ,

$$\epsilon = \sum_{n=0}^{\infty} \Lambda^n \epsilon_n , \tag{7}$$

and the perturbation energies (3) are then given by

$$E_0 = \mathcal{E} + \epsilon_0 \quad , \quad E_n = \epsilon_n 2^{-n/2} \quad (n > 0) \quad . \tag{8}$$

The perturbed equation (5) can be written

$$(H_0 + \Lambda V - \epsilon)\psi = 0 \tag{9}$$

where

$$H_0 = -\tfrac{1}{2}\nabla_r^2 + \tfrac{1}{2}r^2 \quad , \quad V = \frac{1}{r} \quad . \tag{10}$$

The lowest unperturbed solution is

$$\epsilon_0 = \frac{3}{2} \quad , \quad \psi_0 = \pi^{-3/4} e^{-r^2/2} . \tag{11}$$

The nth order perturbation equation is[7]

$$(H_0-\epsilon_0)\psi_n + (V-\epsilon_1)\psi_{n-1} - \sum_{j=1}^{n} \epsilon_j \psi_{n-j} = 0 . \qquad (12)$$

The normalization is chosen so that $\langle \psi, \psi_0 \rangle = 1$ for all λ, or

$$\langle \psi_n, \psi_0 \rangle = \delta_{n0}. \qquad (13)$$

This leads to an especially simple form for the perturbation energies:

$$\epsilon_{n+1} = \langle \psi_0, V \psi_n \rangle \qquad (n \geq 0). \qquad (14)$$

Substitution of $\psi_n = F_n \psi_0$ into (12) leads

$$r F_n'' + 2(1-r^2) F_n' = 2 F_{n-1} - \sum_{j=1}^{n} \epsilon_j F_{n-j} \quad , (n \geq 1). \qquad (15)$$

We seek a solution for F_n in the form of a power series

$$F_n = \sum_{k=0}^{\infty} c_k^{(n)} r^k , \qquad (16)$$

which leads to a recursion relation for the $c_k^{(n)}$ $(n \geq 1,\ k > 0)$,

$$k(k+1) c_k^{(n)} - 2(k-2) c_{k-2}^{(n)} = 2 c_{k-1}^{(n-1)} - 2 \sum_{j=1}^{n} \epsilon_j c_{k-2}^{(n-j)} . \qquad (17)$$

Since ψ_0 is normalized, $F_0 = 1$ and $c_k^{(0)} = \delta_{k0}$, which initiates the recursion. Substitution of (16) into (13) and (14) yields

$$\epsilon_{n+1} = \frac{2}{\sqrt{\pi}} \sum_{k=0}^{\infty} \left(\frac{k}{2}\right)! \, c_k^{(n)}, \tag{18}$$

$$c_0^{(n)} = -\frac{2}{\sqrt{\pi}} \sum_{k=1}^{\infty} \left(\frac{k+1}{2}\right)! \, c_k^{(n)}, \tag{19}$$

where we have used

$$\langle \psi_0, r^k \psi_0 \rangle = \frac{2}{\sqrt{\pi}} \left(\frac{k+1}{2}\right)! \, . \tag{20}$$

For computational purposes it is convenient to re-write the recursion relation (17) in terms of

$$D_k^{(n)} = \frac{2}{\sqrt{\pi}} \left(\frac{k}{2}\right)! \, c_k^{(n)}, \tag{21}$$

which leads to $(k > 0)$

$$(k+1) D_k^{(n)} - (k-2) D_{k-2}^{(n)} = f_{k-1} D_{k-1}^{(n-1)} - \sum_{j=1}^{n} \epsilon_j \, D_{k-2}^{(n-j)}, \tag{22}$$

where

$$f_k = \left(\frac{k-1}{2}\right)! \Big/ \left(\frac{k}{2}\right)! \, . \tag{23}$$

To initiate the recursion we set $D_k^{(0)} = 2\pi^{-\frac{1}{2}}\delta_{k0}$ and calculate $D_k^{(1)}$ for $k \geqslant 1$ from (22). Then $D_0^{(1)}$ can be found from (19), that is

$$D_0^{(n)} = -\frac{2}{\sqrt{\pi}} \sum_{k=1}^{\infty} f_{k+1}^{-1} D_k^{(n)} \qquad (n \geqslant 1), \tag{24}$$

which allows the $D_k^{(2)}$ $(k > 0)$ to be calculated, and so on. The perturbation energies are given by the sum

$$\epsilon_{n+1} = \sum_{k=0}^{\infty} D_k^{(n)} . \tag{25}$$

3. Analytic Results

The first-order energy is

$$\epsilon_1 = \frac{2}{\sqrt{\pi}} = 1.128379167$$

and the first-order coefficients are easily found to be[1]

$$D_k^{(1)} = \frac{(-)^{k+1}\left(\frac{k}{2}-1\right)!}{\sqrt{\pi}\left(\frac{k+1}{2}\right)!} \sim \frac{(-)^{k+1}\,2\sqrt{2/\pi}}{k^{3/2}} \qquad (k>0), \tag{26}$$

$$D_0^{(1)} = -\frac{4}{\pi} \sum_{k=1}^{\infty} \frac{(-)^{k+1}}{k} = -\frac{4}{\pi} \log 2 . \tag{27}$$

By substituting in (25) and summing, or by writing in closed form and integrating[1], it can be shown that

$$\epsilon_2 = -\frac{4}{\pi}\left(\log 2 + 1 - \frac{\pi}{2}\right) = -0.155782 \,, \qquad (28)$$

$$\epsilon_3 = \frac{8}{\pi^{3/2}}\left[2(1-C) + \frac{3}{2}\pi + (\pi+3)\log 2 + \frac{3}{2}(\log 2)^2 - \frac{\pi^2}{24}\right] = +0.0318278 \,, \qquad (29)$$

where C is Catalan's constant.

4. Summation Technique

The series (24) and (25) are alternating in general (as for n = 1, equation (26)) and their finite partial sums oscillate wildly and converge very slowly, typically like $(-)^k/k$ (as for n ≠ 1, equation (27)). The evaluation of the ϵ_n therefore presents a problem, even with a large computer, as a convergence rate of at least k^{-3} is desirable. However, since adjacent partial sums bracket the limit, an average is a better estimate than the partial sums themselves.

Consider the series with partial sum

$$S_N = \sum_{k=0}^{N} D_k \,, \qquad (30)$$

and assume that $\lim_{N\to\infty} S_N = S$ exists. (31)

Define the average

$$\bar{S}_N = \frac{S_N + S_{N-1}}{2},$$

$$= \sum_{k=0}^{N-1} D_k + \tfrac{1}{2} D_N . \qquad (32)$$

Then clearly

$$\lim_{N\to\infty} \bar{S}_N = S . \qquad (33)$$

Although the sequences $\{S_N\}$ and $\{\bar{S}_N\}$ converge together to the same limit S, if the terms D_k alternate in sign, $\bar{S}_N$ is a much better estimate of the limit than S_N. This is because

$$S_N - S_{N-1} = D_N, \text{ whereas } \bar{S}_N - \bar{S}_{N-1} = \frac{D_N + D_{N-1}}{2}. \qquad (34)$$

Thus, for example, if

$$D_k = \frac{(-)^k}{k}, \qquad (35)$$

then

$$\bar{S}_N - \bar{S}_{N-1} = \frac{(-)^N}{2N(N-1)} = O\left(\frac{1}{N^2}\right). \qquad (36)$$

Notice that in this case the difference $\bar{S}_N - \bar{S}_{N-1}$ still alternates,

so that still better estimates may be obtained by averaging the $\bar{S}_N$. Let

$$\bar{\bar{S}}_N = \frac{\bar{S}_N + \bar{S}_{N-1}}{2}$$

$$= \sum_{0}^{N-2} D_k + \frac{3}{4} D_{N-1} + \frac{1}{4} D_N . \qquad (37)$$

Clearly

$$\lim_{N \to \infty} \bar{\bar{S}}_N = S . \qquad (38)$$

However, the sequence $\{\bar{\bar{S}}_N\}$ converges still more rapidly to S . We have

$$\bar{\bar{S}}_N - \bar{\bar{S}}_{N-1} = \frac{D_N + 2D_{N-1} + D_{N-2}}{4} . \qquad (39)$$

If D_k is given by (35), then

$$\bar{\bar{S}}_N - \bar{\bar{S}}_{N-1} = \frac{(-)^N}{2N(N-1)(N-2)} = O\left(\frac{1}{N^3}\right), \qquad (40)$$

which converges fast enough to justify computer treatment.

The evaluations of all the sums in this work were done using equation (37).

5. Computer Program

The program was written in ALGOL and run on a minimum-configuration Burroughs B-5500 Disk System. It is conversive and is run from a remote teletype console. The number of E_n investigated and the number of terms in the partial sums may be varied at run time up to a maximum of 1020, but if they result in creation of more intermediate data than can fit into the computer's actual memory, the program becomes grossly inefficient. Note that since the $D_0^{(n)}$ depend on all the $D_k^{(n)}$ $(k=1,2,\cdots)$, it is necessary to re-run the program to find the effect of adding an extra term to the partial sum.

The method of Section 4 solves the problem of slow convergence, but does not alter the loss of figures inherent in a series whose sum is much smaller than the size of the individual terms. Thus as the E_n get smaller, their accuracy decreases.

The accuracy of the approximation is determined by observing the sensitivity of the approximate E_n to small changes in the number of terms in the summation. The largest number used in calculations through E_8 was 1020 terms, and for E_9 and E_{10} was 501 terms.

Although the twice-averaged sums, (37), still appeared to bracket the limit, there was no advantage to be gained in repeating the averaging, as round-off errors determined the accuracy of the higher E_n. The use of double-precision arithmetic would have reduced the number of possible terms by half.

6. Results and Discussion

Table I presents the calculated E_n, defined by (3), which are believed accurate to the number of figures quoted. The previously found analytic values are listed as a check, and Midtdal's[4] results for the ground state of helium are given for comparison to demonstrate the convergence. Table II lists actual program results to demonstrate the convergence.

In comparing the Hooke and helium results in Table V, it must be remembered that there is an arbitrariness in the choice of the Hook law frequency ω in equation (1). If instead of setting $\omega = Z^2$, we had put $\omega = \Omega Z^2$, then the resulting eigenvalue $E'(\Omega, \lambda)$ would be related to $E(\lambda)$ by

$$E'(\Omega, \lambda) = \Omega E(\lambda \Omega^{-1/2}). \tag{41}$$

The perturbation energies E'_n in the power series expansion in λ would then be related to those for $\Omega = 1$ by

$$E'_n = \Omega^{1-\frac{n}{2}} E_n. \tag{42}$$

A sensible choice for comparing the Hooke and Coulombic 2-electron atoms is $\Omega = 16/9\pi = 0.565884$, which was used by Kestner and Sinanoglu[2]. This value minimizes the 1-election atom energy for a Gaussian trial wave function. However, to compare the rate of convergence the most natural choice is $\Omega = 1/3$, which makes

$E'_0 = 1 = -E_0$. The resulting coefficients E'_n calculated from (42), are given in the third column of Table 1.

The following features emerge from the comparison of the third and fourth columns of Table 1:

(a) The rate of convergence in the Hooke case appears to be a good deal more rapid than for helium.

(b) Whereas the helium E_n are all negative after E_3 , no pattern appears to have set in for the first eleven Hooke E'_n .

(c) Whereas the ratios $r_n = E_n/E_{n-1}$ for the helium increase slowly and steadily after $n = 6$, the Hooke ratios show no pattern.

The asymptotic behaviour of $E(\lambda)$ appears to be[1]

$$E \sim \frac{3}{2^{4/3}}\lambda^{2/3} + \frac{3+\sqrt{3}}{2} + O(\lambda^{-2/3}) \quad , \quad (\lambda \to +\infty), \tag{43}$$

and (compare Stillinger[5])

$$E \sim -\frac{\lambda^2}{4} + \frac{3}{2} + \frac{3}{\lambda^2} + O(\lambda^{-6}) \quad , \quad (\lambda \to -\infty). \tag{44}$$

It is therefore clear that the power series (3) must have a finite radius of convergence, say λ_* . The question arises as to the nature of the singularity at λ_* . Equation (43) suggests that the singularity may be a branch point of order 2/3. Unfortunately the perturbation energies through E_{10} do not appear to provide any information about the singularity. From Midtdal's[4] accurate variational values for the E_n of helium through $n = 21$,

Stillinger[5] was able to deduce the existence of a branch point singularity of order about 6/5 (1.206 ± 0.03) at $\lambda_* = 1.1184 \pm 0.003$. On the other hand, the Hooke model is described essentially by an ordinary differential equation, (5), and should be susceptible to rigorous analysis. Although the Hooke model is bound for all λ, whereas the helium-like atom is unbound for large positive λ, analysis of the λ_* singularity in the Hooke case may help to clarify that in helium.

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Table I

Perturbation energies E_n and E'_n for the ground state of the Hooke atom

Order	Computer E_n	Analytic E_n	E'_n	He atom[4]
0		3	1	-1
1		0.797884561	0.46065886	0.625
2	-0.077890973	-0.07789097267	-0.077890973	-0.157666428
3	0.011252834	0.01125283366	0.019490480	0.008699029
4	-0.001148926		-0.003446778	-0.000888705
5	0.000001268		0.000006588	-0.001036347
6	0.000026767		0.00020409	-0.000612932
7	-0.000004655		-0.00007256	-0.000372184
8	-0.000000079		-0.0000021	-0.000242874
9	0.000000192		0.0000090	-0.000165662
10	-0.000000034		-0.0000028	-0.000116179

Table II

Approximations to perturbation energies $\underline{\underline{E}}_n$ for different numbers of terms N in the partial sums, $\underline{\underline{S}}_N$, equation (37).

N	$E_2 \times 10^2$	$E_3 \times 10^2$	$E_4 \times 10^3$	$E_5 \times 10^6$	$E_6 \times 10^5$
100	-7.78908485410	1.12526012378	-1.14878303211	1.26449906797	2.67204411833
101	-7.78910933470	1.12530595847	-1.14906781640	1.27151475355	2.68128007966
500	-7.78909715430	1.12528315402	-1.14892487711	1.26765368770	2.67669225229
501	-7.78909738230	1.12528361140	-1.14892894354	1.26832315502	2.67678336058
1000	-7.78909725630	1.12528337102	-1.14892632238	1.26844883275	2.67671711775
1001	-7.78909728610	1.12528340986	-1.14892716751	1.26771705411	2.67669718809
1019	-7.78909728520	1.12528340968	-1.14892716070	1.26790687200	2.67669057471
1020	-7.78909725770	1.12528336387	-1.14892641832	1.26836827320	2.67671757995

N	$E_7 \times 10^6$	$E_8 \times 10^8$	$E_9 \times 10^7$	$E_{10} \times 10^8$
100	-4.62289896219	-8.91074307640	1.93498345329	-3.37792709345
101	-4.68546290117	-6.84783856260	1.90933944719	-3.47519697288
500	-4.65465003008	-7.90970258150	1.92018469128	-3.43685124768
501	-4.65455382237	-7.84257263540	1.92024660316	-3.44665380665
1000	-4.65515909425	-7.90145921990		
1001	-4.65482415962	-7.85394593770		
1019	-4.65507882614	-7.87697587120		
1020	-4.65523129838	-7.93147094630		

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